

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵: C08G 69/26, 69/28	A1	(11) International Publication Number: WO 94/29367 (43) International Publication Date: 22 December 1994 (22.12.94)
(21) International Application Number: PCT/CA94/00324 (22) International Filing Date: 8 June 1994 (08.06.94) (30) Priority Data: 9311754.7 8 June 1993 (08.06.93) GB (71) Applicant: DUPONT CANADA INC. [CA/CA], Box 2200 Streetsville, Mississauga, Ontario L5M 2H3 (CA). (72) Inventor: LEBOEUF, Christian, 19 1/2 Montgomery Boulevard, Kingston, Ontario K7M 3N4 (CA). (74) Agent: GALLOWAY, Warren, J.; Sim & McBurney, Suite 701, 330 University Avenue, Toronto, Ontario M5G 1R7 (CA).		(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HIGH PRESSURE PROCESS FOR THE MANUFACTURE OF TEREPHTHALIC ACID COPOLYAMIDES (57) Abstract A process for the copolymerization of (1) a carboxylic acid comprising terephthalic acid and mixtures thereof with isophthalic acid with (2) a mixture of hexamethylene diamine and 2-methyl pentamethylene diamine. The pressure in the polymerization process is maintained at at least about 2.15 MPa for a period of at least about 40 minutes so that the resultant copolyamide, when annealed, has less than 1 % by weight based on the total weight of the copolyamide of fractions having melting points greater than 320 °C. Use of lower pressures and times tends to result in formation of a high melting fraction.		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

HIGH PRESSURE PROCESS FOR THE
MANUFACTURE OF TEREPHTHALIC ACID COPOLYAMIDES

The present invention relates to a process for the manufacture of copolyamides of terephthalic acid, and especially to the manufacture of such copolyamides without formation of a high melting fraction by using a high pressure polymerization process.

As used herein, a "single step" polymerization process is a polymerization process in which monomers are subjected to a polymerization cycle in a reactor that concludes with the pressure being returned to substantially atmospheric pressure. It is understood that the copolyamide obtained from such a process may be subjected to further processing, including finishing and extrusion, before or after pelletization.

Single-step polymerization processes have the advantage that polymer is manufactured in a single step, as opposed to two step or multi-step processes, thereby reducing handling of the partially formed polymer during the intermediate stages of the process. However, in the manufacture of copolyamides of terephthalic acid, especially copolyamides of terephthalic acid, hexamethylene diamine and 2-methyl pentamethylene diamine, using a single step polymerization process, it has been found that a high melting fraction is formed.

The high melting fraction, with a melting point in excess of 320°C and especially approximately 334°C, is usually not noticed in the first batch of polymer produced in an autoclave, but becomes apparent in subsequent batches made in the same autoclave unless steps are taken to carefully clean-out the autoclave between consecutive batches. As the polymer would normally be subsequently processed at melt temperatures of less than 320°C, the high melting fraction manifests itself as unmelted or gel-like portions of polymer, which are commercially unacceptable; the gel-like portions are believed to be essentially comprised of a high melting crystalline phase, which is soluble in sulphuric acid, and not gel per se which would not be soluble in sulphuric acid.

It has now been found that copolymers of terephthalic

SUBSTITUTE SHEET

- 2 -

acid, optionally including isophthalic acid, and mixtures of hexamethylene diamine and 2-methyl pentamethylene diamine, may be manufactured without the formation of a high melting fraction in significant amounts.

5 Accordingly, the present invention provides a process for the preparation of a copolyamide, especially partially crystalline copolyamide, comprising the polymerization stages of:

10 (a) feeding to a reactor an aqueous salt solution of an admixture of aromatic carboxylic acid and aliphatic diamine, said aromatic carboxylic acid being selected from terephthalic acid and mixtures of terephthalic acid and isophthalic acid and said aliphatic diamine being a mixture of hexamethylene diamine and 2-methyl pentamethylene diamine;

15 (b) heating the aqueous salt solution under a pressure of at least about 2.15 MPa for a period of at least about 40 minutes, especially at least 60 minutes, and venting water and other volatile matter from the reactor;

20 (c) reducing the pressure in the reactor to atmospheric pressure;

(d) controlling stages (b) and (c) so as to avoid excessive foaming of the admixture in the reactor; and

(e) discharging the copolyamide so obtained from the reactor.

25 In a preferred embodiment of the process of the invention, stage (c) additionally includes maintaining the admixture in the reactor under a vacuum.

In another embodiment, the pressure in stage (b) is at least 2.28 MPa.

30 In a further embodiment, the time in stage (b) is at least 90 minutes.

The present invention further provides in a process for the preparation of multiple consecutive batches of a copolyamide, especially partially crystalline copolyamide, of
35 terephthalic acid and hexamethylene diamine in a reactor without clean-out of the reactor, in which the copolyamide obtained from such process contains more than about 2% by

SUBSTITUTE SHEET

- 3 -

weight of a fraction with an annealed melting point of greater than 320°C, said process comprising the stages of:

- (a) feeding to a reactor an aqueous salt solution of an admixture of aromatic carboxylic acid and aliphatic diamine, said aromatic carboxylic acid being selected from terephthalic acid and mixtures of terephthalic acid and isophthalic acid and said aliphatic diamine being a mixture of hexamethylene diamine and 2-methyl pentamethylene diamine;
 - (b) heating the aqueous salt solution under pressure and venting water and other volatile matter from the reactor;
 - (c) reducing the pressure in the reactor to atmospheric pressure;
 - (d) controlling stages (b) and (c) so as to avoid excessive foaming of the admixture in the reactor; and
 - (e) discharging the copolyamide so obtained from the reactor;
- the improvement comprising maintaining the pressure in stage (b) at at least about 2.15 MPa.

In a preferred embodiment, the pressure of at least about 2.15 MPa is maintained in stage (b) for a period of at least about 40 minutes, especially at least 60 minutes.

In preferred embodiments of the processes of the invention, the stages of the process are controlled so that the copolyamide produced has an inherent viscosity of at least 0.6 dL/g, especially at least 0.8 dL/g.

As used herein, "clean-out" of a reactor means steps taken to clean or remove high molecular weight polyamide, degradation or gel products and other matter that is not discharged from the reactor under normal processing conditions.

The present invention relates to the manufacture of partially crystalline copolyamides formed from an aromatic carboxylic acid and a mixture of hexamethylene diamine and 2-methyl pentamethylene diamine. The aromatic carboxylic acid is terephthalic acid or a mixture of terephthalic acid and isophthalic acid.

The amounts of acid and diamines should be substantially

SUBSTITUTE SHEET

- 4 -

complementary on a molar basis, as will be appreciated by persons skilled in the art. An excess of acids or diamines, especially the latter, may be used depending on the desired characteristics of the copolyamide and the nature and extent of side reactions that may produce volatile or other matter; as noted below, diamines tend to be more volatile than acids. A broad range of ratios of amounts of terephthalic acid, isophthalic acid, hexamethylene diamine and 2-methyl pentamethylene diamine may be used in the process. In preferred embodiments, the ratio of hexamethylene diamine to 2-methyl pentamethylene diamine is in the range 40:60 to 60:40, and especially about 50:50, with the acid being terephthalic acid. In other embodiments, the amount of isophthalic acid is selected to be at least 27.5%, molar basis, especially at least 30%, of the total amount of acid and diamine monomers.

The copolyamides produced by the process of the present invention are generally partially crystalline polymers, rather than an amorphous polymer. In embodiments, the polymers have a heat of fusion of greater than 17 J/g. Crystallinity may be determined using a differential scanning calorimeter.

The copolyamide is prepared in a polymerization process in which an aqueous salt solution of the aromatic carboxylic acids, hexamethylene diamine and 2-methyl pentamethylene diamine is fed to a reactor. The molar amount of aromatic acid is substantially complementary to the total molar amount of the diamines, as discussed above. As is known, diamines tend to be more volatile than carboxylic acids and thus it may be desirable to feed an excess of diamine to the reactor. Catalysts may also be used e.g. phosphinic acid and/or the sodium or potassium salts thereof, phosphorus acid, hypophosphorous acid, sodium hypophosphite, phosphoric acid and the like; typical amounts of catalysts are 0.02-1.00% by weight, especially 0.025-0.20% by weight.

In the process, the aqueous salt solution is heated in a reactor (autoclave) under pressure. The process of the present invention requires that the pressure be maintained at

SUBSTITUTE SHEET

- 5 -

at least about 2.15 MPa, although the pressure may also be maintained at a lower pressure for a period of time, especially prior to maintaining at the pressure of at least 2.15 MPa. In preferred embodiments, the pressure is
5 maintained at at least about 2.22 MPa and preferably at least about 2.28 MPa. In addition, the pressure is preferably maintained at such values for at least 60 minutes, especially at least 90 minutes and in particular embodiments for at least 120 minutes. Water and other volatile matter, which may
10 include diamine, is vented from the reactor. The temperature of the admixture in the reactor will normally exceed at least 275°C, and especially be in the range of 300-315°C.

The pressure in the reactor is then reduced to atmospheric pressure, especially over a period of at least 15
15 minutes, particularly over a period of 20 to 90 minutes. The pressure should be reduced in a manner that minimizes or avoids excessive foaming of the reaction mixture in the reactor. Anti-foam agents may be added to reduce the amount of foaming. The reaction mixture is then maintained at about
20 atmospheric pressure or under a vacuum until the copolyamide has reached a predetermined molecular weight. The copolyamide thus obtained is discharged from the reactor. It should be understood, however, that the copolyamides may be manufactured using continuous polymerization techniques and/or subjected to
25 solid phase polymerization or other further processing stages.

As is illustrated herein, the use of a polymerization process such as that described above will often result in the formation of a high melting fraction of copolyamide, with a
30 melting point after annealing of greater than about 320°C, and especially in the range of about 335-340°C, unless the pressure and time are maintained within the limits given above. It is to be understood however, that certain ratios of monomer compositions will result in copolyamides that do not
35 contain the high melting fraction, as discussed in the aforementioned application of R.R. Soelch. The high melting fraction will normally not be apparent in the first batch of

SUBSTITUTE SHEET

copolyamide formed in an autoclave i.e. the first batch formed after the autoclave has been thoroughly cleaned. The high melting fraction will normally appear, if it is going to appear, in the second or third batches of copolyamide formed in the autoclave. It is not practical or economic to clean out an autoclave after each and every batch of copolyamide has been produced.

In order to prevent formation of the high melting fraction, or to at least reduce the amount of high melting fraction to less than 2% by weight, and especially less than 0.05% by weight, the pressure during reaction is maintained at at least about 2.15 MPa, especially at least 2.28 MPa, for at least about 40 minutes, preferably for a period of 40 to 120 minutes. The effects of use of lower pressures or shorter times is illustrated in the examples. The copolyamides of the invention may be blended with stabilizers, flame retardants, smoke depressants, plasticizers, conductive and/or anti-static agents, lubricants and mould release agents, nucleating agents, dyes and pigments, fillers including glass fibres, minerals, toughening and other modifying agents, and other additives that may be used in polyamide compositions. Examples of heat stabilizers include copper(I) halides e.g. bromide and iodide, and alkali halides e.g. lithium, sodium and potassium bromides and iodides, which may be used with or without phosphorus compounds. Examples of the latter are phosphites, phosphines, phosphates and alkali metal salts of phosphorus acids e.g. sodium phenyl phosphinate, sodium hypophosphite, triaryl- and tris(alkylaryl) phosphines e.g. tri-n-butyl phosphine, phenyl dimethyl phosphine and triphenyl phosphine. The organic heat stabilizers include hindered phenols and hindered amines, as well as UV stabilizers and phenolic metal deactivators. Nucleating agents include talc, calcium fluoride and salts of phosphorus acids, for example sodium phenyl phosphinate.

A wide range of fillers may be used e.g. in amounts of 0.5-200 parts of filler per 100 parts of copolyamide. Examples of such fillers include, but are not limited to,

SUBSTITUTE SHEET

- 7 -

silica, metasilicates, alumina, talc, diatomaceous earth, clay, kaolin, quartz, glass, mica, titanium dioxide, molybdenum disulphide, gypsum, iron oxide, zinc oxide, fibres e.g. glass, carbon, boron, aromatic and ceramic fibres, powdered polytetrafluoroethylene and the like.

The copolyamides may be used in the manufacture of products using melt processing techniques, especially products intended for use at temperatures that are higher than those typically used with other polyamides. For example, the copolyamides may be formed into articles using injection moulding technology e.g. into valves, tanks, containers, washers and the like for automotive end-uses, into articles for electrical end-uses e.g. parts requiring resistance to temperatures of 260°C or above, and articles where retention of mechanical properties under the influence of heat, moisture, hydrocarbons, alcohols including so-called gasohol, and the like are important. Alternatively, the polymers may be spun into fibres e.g. for sewing or industrial threads for end-uses where low shrinkage and elongation are important and/or retention of properties under the influence of moisture, hydrocarbons, alcohols and the like is important. The copolyamides may also be formed into film and sheet. Barrier properties of the copolyamides to water and oxygen may also find uses. The copolyamides may be particularly useful for end-uses where retention of properties at elevated temperatures is required, including as retortable containers.

In embodiments of the invention, the copolyamide is in the form of a fibre, or filament. The fibre preferably has a tenacity of at least 1.5 g/denier and a modulus of at least 30 g/denier.

The present invention is illustrated by the following examples.

Example I

A series of runs were carried out in a 12L reaction vessel. The procedures used are illustrated by the following: Procedure A, as used in Run 1D:

The 12L reaction vessel, equipped with a helical ribbon

SUBSTITUTE SHEET

agitator, was charged with 2659g (16.02 moles) of terephthalic acid, 976g (8.41 moles) of 2-methyl pentamethylene diamine, 1268.4g of 74.74% (weight basis) of aqueous hexamethylene diamine solution (8.17 moles), 3.94g of 25% (weight basis) of aqueous sodium hypophosphite solution, 6ml of 10% (weight basis) Carbowax® 3350 polyethylene glycol in water and 1200g of demineralized water.

With the agitator rotating at 50 rpm, the mixture was heated to 130°C, vented to remove entrained oxygen and then heated to 225°C. With the reaction pressure maintained at 1.70 MPa, volatile matter was released over a period of 88 minutes, during which period of time the temperature of the reaction mixture rose to 300°C. The pressure in the reaction mixture was then reduced to atmospheric pressure over a period of 60 minutes, the temperature in the reaction mixture rising to 318°C. The rate of agitation was reduced to 5 rpm. The reaction mixture was maintained under a vacuum of 40kPa for 15 minutes and then the polymer obtained was discharged from the reactor and quenched in a water bath.

The polymer obtained had an inherent viscosity (IV) of 0.90 dL/g; inherent viscosity was measured on a 5.0g/L solution in m-cresol. The polymer had a single melting point of 302.4°C, as measured by differential scanning calorimetry (DSC). The polymer obtained in this example, which is a comparative example, exhibited visually the presence of a higher melting fraction, when the polymer was extruded in the form of a strand, but the high melt fraction was less than the detection limit in DSC i.e. it was less than about 0.5% by weight.

Procedure B, as used in Run 2C

The 12L reaction vessel was charged with 2322g (14.00 moles) of terephthalic acid, 892g (7.69 moles) of 2-methyl pentamethylene diamine, 1162.9g of 72.58% (weight basis) of aqueous hexamethylene diamine solution (7.28 moles), 3.94g of 25% (weight basis) of aqueous sodium hypophosphite solution, 6ml of 10% (weight basis) Carbowax® 3350 polyethylene glycol in water, 1200g of demineralized water and 500g of pellets of

SUBSTITUTE SHEET

- 9 -

a polymer of terephthalic acid and a 50:50 mixture of hexamethylene diamine and 2-methyl pentamethylene diamine which contained about 18% by weight of a high melting fraction; this polymer was added to simulate an annealed polymer residue and it was the only way this could be achieved in the reaction vessel being used due to equipment limitations.

Copolyamide was produced using the method of Procedure A above, except that the second polymerization cycle, venting at constant pressure, was conducted at a pressure of 2.39 MPa for a period of 66 minutes.

The copolyamide obtained had an IV of 0.81 dL/g and a melting point of 302.6°C. The polymer did not exhibit a high melt fraction when observed visually but it showed a high melt fraction of about 2.8% by weight when tested with DSC.

Table I reports the results of series of runs made using Procedure A or Procedure B above, depending on whether polymer was added to the reaction vessel. Runs 1A-1E are comparative runs and Runs 2A-5D illustrate the invention.

The Runs illustrate, in particular, the effect of pressure in stage (b), the effect of time in stage (b) and the effect of added polymer containing high melt fraction.

SUBSTITUTE SHEET

- 10 -

TABLE I

	RUN NO.	1A	1B	1C	1D	1E
	P ₂ (MPa)	1.70	1.70	1.70	1.70	1.70
5	T ₃ (°C)	275	275	275	300	300
	RESIDUE(g)	0	0	0	0	500
	t ₂ (min)	60	60	120	120	60
	IV (dL/g)	0.80	0.81	0.63	0.90	0.79
	3MP (eq/MMg)	56	56	74	66	64
10	HIGH MELT, (% , DSC)	<0.5	<0.5	1.8	<0.5	15.1
	HIGH MELT (VISUAL)	NO	NO	YES	YES	YES
	% OUT	86	80	53	80	15

TABLE I (cont.)

	RUN NO.	2A	2B	2C	2D	2E	2F
	P ₂ (MPa)	2.39	2.39	2.39	2.39	2.39	2.39
	T ₃ (°C)	300	300	300	300	300	300
	RESIDUE(g)	0	0	500	500	1000	1000
20	t ₂ (min)	60	120	60	120	60	120
	IV (dL/g)	0.83	0.81	0.81	0.78	0.80	0.63
	3MP (eq/MMg)	83	110	94	104	90	108
	HIGH MELT (% , DSC)	<0.5	<0.5	2.8	4.5	7.0	13.0
	HIGH MELT (VISUAL)	NO	NO	NO	NO	NO	NO
25	% OUT	85	86	62	39	43	41

SUBSTITUTE SHEET

- 11 -

TABLE I (cont.)

RUN NO.	TABLE I (cont.)			
	3A	3B	3C	3D
P ₂ (MPa)	2.49	2.49	2.49	2.49
5 T ₃ (°C)	300	300	300	300
RESIDUE(g)	0	0	1000	1000
t ₂ (min)	60	120	60	120
IV (dL/g)	0.74	0.70	0.69	0.62
3MP (eq/MMg)	109	116	113	116
10 HIGH MELT (% DSC)	<0.5	<0.5	<0.5	4.3
HIGH MELT (VISUAL)	NO	NO	NO	NO
% OUT	85	87	88	63

TABLE I (cont.)

RUN NO.	TABLE I (cont.)					
	4A	4B	4C	4D	4E	4F
P ₂ (MPa)	2.63	2.63	2.63	2.63	2.63	2.63
T ₃ (°C)	300	300	300	300	300	300
RESIDUE(g)	0	0	500	500	1000	1000
20 t ₂ (min)	60	120	60	120	60	120
IV (dL/g)	0.74	0.70	0.53	0.68	0.69	0.69
3MP (eq/MMg)	121	134	112	128	107	114
HIGH MELT (% DSC)	<0.5	<0.5	1.5	1.9	2.6	5.8
HIGH MELT (VISUAL)	NO	NO	NO	NO	NO	NO
25 % OUT	85	90	74	76	80	53

SUBSTITUTE SHEET

TABLE I (cont.)

RUN NO.		5A	5B	5C	5D
5	P ₂ (MPa)	3.07	3.07	3.07	3.07
	T ₃ (°C)	300	300	300	300
	RESIDUE(g)	0	0	1000	1000
	t ₂ (min)	120	120	120	120
	IV (dL/g)	0.57	0.55	0.54	0.52
10	3MP (eq/MMg)	174	190	176	186
	HIGH MELT (% DSC)	<0.5	<0.5	2.9	4.5
	HIGH MELT (VISUAL)	NO	NO	NO	NO
	% OUT	85	89	81	82

- Note:
- 15 "P₂" is the pressure in stage (b);
 "T₃" is the temperature at the start of stage (c);
 "Residue" is the amount of polymer containing high melt fraction added to the reaction vessel;
 "t₂" is the time in stage (b);
 "IV" is inherent viscosity measured on a 5.0 g/L solution in m-cresol;
- 20 "3MP" is the amount of cyclic amine produced in the process, referred to as the amount of 3-methyl piperidine;
- 25 "High Melt % DSC" is the amount of high melting fraction as determined by differential scanning calorimetry;
- "High Melt Visual" indicates whether the high melt fraction was visible in an extruded strand of polymer;
- 30 "% Out" is the amount of polymer cast from the reaction vessel, expressed as a percentage of the stoichiometric amount.

The results show that the high melt fraction was visible in the polymer when the pressure in stage (b) was low i.e. Runs 1A-1E. The Runs at higher pressure did not exhibit visual high melting fraction even when polymer containing high melt fraction had been added to the reaction vessel.

SUBSTITUTE SHEET

- 13 -

Increasing the period of time in stage (b) from 60 minutes to 120 minutes had an adverse affect on the amount of high melt fraction as determined by DSC.

5 The addition of polymer containing high melt fraction to the reaction vessel, to simulate presence of polymer with high melt fraction remaining in the vessel from a previous run, adversely affected the amount of polymer cast from the reaction vessel, especially with the higher viscosity polymers.

10 The melting point of the high melt fraction is in excess of the temperatures reached during the polymerization process. Thus, it is to be expected that the high melt fraction added in the form of pellets containing that fraction would not be destroyed during the polymerization process. Moreover, it
15 might be anticipated that the presence of the crystalline high melt fraction would induce crystallization of additional polymer into the crystalline form of the high melt fraction. Consequently, it would be expected that presence of high melt fraction in the reactor prior to polymerization would result
20 in an increase in that fraction in the polymer obtained.

This example shows that use of the high pressure resulted in a lower increase in high melt fraction, and in some instances a decrease in the amount, compared with the higher amounts obtained when the lower pressure was used. This has
25 significant benefits in the operation of the polymerization process to produce multiple consecutive batches of polymer of commercially-acceptable quality without cleanout of the reactor or autoclave.

Example II

30 An aqueous salt solution formed from terephthalic acid, hexamethylene diamine and 2-methyl pentamethylene diamine (1112.32 kg, 44.8% salt with a 5.2% molar excess of hexamethylene diamine and 13% molar excess of 2-methyl pentamethylene diamine) was charged to an autoclave. The
35 solution was heated in the autoclave, with venting of water at a constant pressure of 340kPa until the salt in the autoclave reached a temperature of 162°C. Venting was then interrupted.

SUBSTITUTE SHEET

- 14 -

The temperature of the autoclave was increased, with gases being vented at a pressure of 2.15 MPa; the autoclave was maintained at this pressure for approximately two hours, until the temperature of the melt had reached 300°C. A pressure reduction cycle was then initiated, to atmospheric pressure over a period of about 60 minutes. During this stage, the melt reached 318°C. The molten polymer was then subjected to a vacuum of 80 kPa for 17 minutes, the melt temperature increasing to 330°C.

The polymer thus obtained was discharged from the autoclave through a multiple hole die, quenched in cold water and pelletized. The yield of pelletized polymer was 88.2%.

The polymer obtained had an inherent viscosity (IV) of 0.87 dL/g, as measured on a 5.0g/L solution of polymer in m-cresol. The polymer had a single melting point of 302°C (DSC). The polymer did not show any visual evidence of high melt fraction, and none (<0.5%) was detected by DSC. The amount of cyclic amine (3-MP) was 88 eq/MMg of polymer.

Example III

The procedure of Example II was repeated using lower pressures and temperatures.

The aqueous salt solution was charged to an autoclave and heated with venting of water at a constant pressure of 240kPa until the salt in the autoclave reached a temperature of 145°C. Venting was then interrupted. The temperature of the autoclave was increased, with gases being vented at a pressure of 1.70 MPa; the autoclave was maintained at this pressure for approximately two hours, until the temperature of the melt had reached 295°C. The pressure reduction cycle was then initiated, to atmospheric pressure over a period of about 60 minutes. During this stage, the melt reached 312°C. The molten polymer was then subjected to a vacuum of 80 kPa for 10 minutes, the melt temperature increasing to 318°C.

The polymer thus obtained was discharged from the autoclave through a multiple hole die, quenched in cold water and pelletized. However, discharging of the polymer from the autoclave lasted for only a short period of time and the yield

SUBSTITUTE SHEET

- 15 -

of pelletized polymer was only 66.5%.

The polymer obtained had an inherent viscosity (IV) of 0.81 dL/g, as measured on a 5.0g/L solution of polymer in m-cresol. The polymer had a single melting point of 302°C (DSC). The polymer showed visual evidence of high melt fraction; the amount detected using DSC was approximately 4.5%. The amount of cyclic amine (3-MP) was 74 eq/MMg of polymer.

Example IV

10 An aqueous salt solution formed from terephthalic acid, hexamethylene diamine and 2-methyl pentamethylene diamine (2540 kg, 50% salt with a 5.4% molar excess of hexamethylene diamine and 7.4% molar excess of 2-methyl pentamethylene diamine) was charged to an autoclave. The solution was heated
15 in the autoclave, with venting of water at a constant pressure of 340kPa until the salt in the autoclave reached a temperature of 162°C. Venting was then interrupted. The temperature of the autoclave was increased, with gases being vented at a pressure of 2.15 MPa; the autoclave was maintained
20 at this pressure for approximately two hours, until the temperature of the melt had reached 300°C. A pressure reduction cycle was then initiated, to atmospheric pressure over a period of about 40 minutes. During this stage, the melt reached 323°C. The molten polymer was then subjected to
25 a vacuum of 80kPa for 4 minutes, the melt temperature increasing to 325°C.

The polymer thus obtained was discharged from the autoclave through a multiple hole die, quenched in cold water and pelletized. The yield of pelletized polymer was 77%.

30 The polymer obtained had an inherent viscosity (IV) of 0.84 dL/g, as measured on a 5.0g/L solution of polymer in m-cresol. The polymer had a single melting point of 302°C (DSC). The polymer did not show any visual evidence of high melt fraction; the amount detected by DSC was approximately
35 1.4% by weight. The amount of cyclic amine (3-MP) was 86 eq/MMg of polymer.

SUBSTITUTE SHEET

- 16 -

CLAIMS:

1. A process for the preparation of a copolyamide, comprising the polymerization stages of:

5 (a) feeding to a reactor an aqueous salt solution of an admixture of aromatic carboxylic acid and aliphatic diamine, said aromatic carboxylic acid being selected from terephthalic acid and mixtures of terephthalic acid and isophthalic acid and said aliphatic diamine being a mixture of hexamethylene diamine and 2-methyl pentamethylene diamine;

10 (b) heating the aqueous salt solution under a pressure of at least about 2.15 MPa for a period of at least about 40 minutes, and venting water and other volatile matter from the reactor;

15 (c) reducing the pressure in the reactor to atmospheric pressure;

(d) controlling stages (b) and (c) so as to avoid excessive foaming of the admixture in the reactor; and

(e) discharging the copolyamide so obtained from the reactor.

20

2. The process of Claim 1 in which the pressure in stage (b) is at least about 2.28 MPa.

25 3. The process of Claim 1 or Claim 2 in which the time in stage (b) is at least 60 minutes.

4. The process of Claim 3 in which the time in stage (b) is at least about 90 minutes.

30

5. A process for the preparation of multiple consecutive batches of a copolyamide of terephthalic acid and hexamethylene diamine in a reactor without clean-out of the reactor, in which the copolyamide obtained from such process contains more than about 2% by weight of a fraction with an annealed melting point of greater than 320°C, said process

35 comprising the stages of:

(a) feeding to a reactor an aqueous salt solution of an

SUBSTITUTE SHEET

- 17 -

admixture of aromatic carboxylic acid and aliphatic diamine, said aromatic carboxylic acid being selected from terephthalic acid and mixtures of terephthalic acid and isophthalic acid and said aliphatic diamine being a mixture of hexamethylene diamine and 2-methyl pentamethylene diamine;

(b) heating the aqueous salt solution under pressure and venting water and other volatile matter from the reactor;

(c) reducing the pressure in the reactor to atmospheric pressure;

(d) controlling stages (b) and (c) so as to avoid excessive foaming of the admixture in the reactor; and

(e) discharging the copolyamide so obtained from the reactor;

the improvement comprising maintaining the pressure in stage (b) at at least about 2.15 MPa.

6. The process of Claim 5 in which the pressure of at least about 2.15 MPa is maintained in stage (b) for a period of at least about 40 minutes.

7. The process of Claim 6 in which the pressure is maintained in stage (b) for at least about 60 minutes.

8. The process of any one of Claims 1-7 in which stage (c) additionally includes maintaining the admixture in the reactor under a vacuum.

9. The process of any one of Claims 1-8 in which the stages of the process are controlled so that the copolyamide produced has an inherent viscosity of at least about 0.6 dL/g.

10. The process of any one of Claims 1-8 in which the stages of the process are controlled so that the copolyamide produced has an inherent viscosity of at least about 0.8 dL/g.

11. The process of any one of Claims 1-10 in which the copolyamide is a partially crystalline copolyamide.

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA 94/00324A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08G69/26 C08G69/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 10525 (DU PONT CANADA) 25 June 1992 ---	
A	EP,A,0 540 890 (HOECHST CELANESE) 12 May 1993 ---	
A	EP,A,0 384 859 (RHONE-POULENC) 29 August 1990 ---	
A	WO,A,91 15537 (RHONE-POULENC) 17 October 1991 ---	
A	FR,A,2 325 673 (DYNAMIT NOBEL) 22 April 1977 ---	
A	FR,A,2 355 043 (DYNAMIT NOBEL) 13 January 1978 -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

& document member of the same patent family

Date of the actual completion of the international search

17 October 1994

Date of mailing of the international search report

- 9. 11. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31-651 epo nl
Fax (+ 31-70) 340-3016

Authorized officer

Leroy, A

INTERNATIONAL SEARCH REPORT

information on patent family members

International application No.

PCT/CA 94/00324

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9210525	25-06-92	AU-A- 9064491 EP-A- 0561886 FI-A- 932690 JP-T- 6503590	08-07-92 29-09-93 11-06-93 21-04-94
EP-A-0540890	12-05-93	NONE	
EP-A-0384859	29-08-90	FR-A- 2643377 AU-A- 4987590 CA-A- 2007568 JP-A- 2247224 JP-B- 6062761 US-A- 5336754 US-A- 5109106	24-08-90 30-08-90 21-08-90 03-10-90 17-08-94 09-08-94 28-04-92
WO-A-9115537	17-10-91	FR-A- 2660316 EP-A- 0522027 US-A- 5322923	04-10-91 13-01-93 21-06-94
FR-A-2325673	22-04-77	DE-A- 2542938 BE-A- 846558 CA-A- 1063293 GB-A- 1557272 JP-A- 52041692 SE-A- 7610546 US-A- 4111921	07-04-77 17-01-77 25-09-79 05-12-79 31-03-77 27-03-77 05-09-78
FR-A-2355043	13-01-78	DE-A- 2627342 GB-A- 1579274 JP-A- 52155698 US-A- 4163101	22-12-77 19-11-80 24-12-77 31-07-79

THIS PAGE BLANK (USPTO)

This Page is inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images
problems checked, please do not report the
problems to the IFW Image Problem Mailbox**

THIS PAGE BLANK (USPTO)